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Relaxation rate distribution from frequency or time dependent data

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Abstract

A method for the inversion of experimental susceptibility spectra or relaxation functions in terms of a spectrum of relaxation times is proposed. The method uses the Boas–Widder formula for the inversion of the Laplace transform for real variables. The method is tested numerically on known spectra for the Cole–Cole, Cole–Davidsson and Kohlrausch–Williams–Watts models as well as for more complex spectra obtained from the mode-coupling theory, and in all cases the agreement is very good.

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1. Introduction

The dielectric properties of materials have been extensively studied for many years, in such diverse fields as physics, chemistry, engineering, biology etc. [1–8]. In many of these systems one finds rather complex spectra with very broad loss peaks which indicates a very broad distribution of relaxation times. A central issue is to understand the origin of this broad distribution and relate it to the properties of the material on a microscopic level.

The relaxation properties of materials is often described via a relaxation function $\phi(t)$, which then can be expressed in terms of a distribution of relaxation rates as

$$\phi(t) = \int_0^\infty \mathrm{e}^{-ut}\rho(u)\,\mathrm{d}u = \int_0^\infty \mathrm{e}^{-t/\tau} g(\tau)\,\mathrm{d}\ln\tau, \tag{1}$$

where $g(\tau) = \rho(1/\tau)/\tau$. For the long time or small frequency region of interest here we have $g(\tau) > 0$ and (1) then imply that the relaxation function $\phi(t)$ is a completely monotonic function [9]

$$(-1)^n \frac{\mathrm{d}^n}{\mathrm{d}t^n}\phi(t) \geqslant 0,$$

i.e., the system has no oscillatory motions on these time or frequency scales.

The Laplace transform of $\phi(t)$ is given by

$$\hat{\phi}(z) = \int_0^\infty \mathrm{e}^{-zt}\phi(t)\,\mathrm{d}t = \int_0^\infty \frac{\rho(u)}{z+u}\,\mathrm{d}u = \int_0^\infty \frac{g(\tau)}{z\tau+1}\,\mathrm{d}\tau$$

and this determines the corresponding complex dielectric constant $\epsilon(z)$ or the susceptibility $\chi(z)$ by way of

$$\begin{aligned}\epsilon(z) &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\int_0^\infty \mathrm{e}^{-zt}\left(-\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}\right)\mathrm{d}t \\ &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\left[1 - z\hat{\phi}(z)\right] \\ &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\chi(z).\end{aligned} \tag{2}$$

Here ϵ_0 is the static dielectric constant for $\omega = 0$ and ϵ_∞ the corresponding one for high frequencies. In terms of the distribution function $g(\tau)$ we then obtain

$$\frac{\epsilon(z) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \chi(z) = \int_0^\infty \frac{g(\tau)}{1+z\tau}\,\mathrm{d}\ln\tau \tag{3}$$

from which we get the real and imaginary parts χ' and χ'' by setting $z = \mathrm{i}\omega$

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$$\chi'(\omega) = \int_0^\infty \frac{g(\tau)}{1+(\omega\tau)^2}\,\mathrm{d}\ln\tau$$
$$\chi''(\omega) = \int_0^\infty \frac{\omega\tau g(\tau)}{1+(\omega\tau)^2}\,\mathrm{d}\ln\tau \tag{4}$$

A basic problem is to invert these relations, i.e., to obtain the relaxation spectrum $g(\tau)$ from a knowledge of either the relaxation function $\phi(t)$ or the dielectric constant $\epsilon(z)$ or rather the real or imaginary parts $\epsilon'(\omega)$ and $\epsilon''(\omega)$. There exist several methods to accomplish this both analytically [9–15] and numerically [16–22]. From the Laplace transform $\hat{\phi}(z)$ and the resulting expressions for the real and imaginary parts $\hat{\phi}(z = \mathrm{i}\omega) = \phi'(\omega) - \mathrm{i}\phi''(\omega)$ one obtains directly [11–14]

$$\rho(u) = \pm\frac{1}{\pi}\mathrm{Im}\,\hat{\phi}(u\mathrm{e}^{\mp\mathrm{i}\pi}) = \pm\frac{1}{\pi u}\mathrm{Im}\,\chi(u\mathrm{e}^{\mp\mathrm{i}\pi}), \tag{5}$$

$$\rho(u) = \mp\frac{2}{\pi}\mathrm{Im}\,\phi'(u\mathrm{e}^{\pm\mathrm{i}\pi/2}) = \frac{2}{\pi u}\mathrm{Re}\,\chi''(u\mathrm{e}^{\pm\mathrm{i}\pi/2}), \tag{6}$$

$$\rho(u) = \frac{2}{\pi}\mathrm{Re}\,\phi''(u\mathrm{e}^{\pm\mathrm{i}\pi/2}) = \mp\frac{2}{\pi u}\mathrm{Im}\,\chi'(u\mathrm{e}^{\pm\mathrm{i}\pi/2}). \tag{7}$$

These relations gives the distribution $\rho(u)$ or $g(\tau)$ as an analytic continuation of the frequency dependent dielectric constant to the negative real or the imaginary axis. However, to use these expressions one must first find an analytical representation of the experimental data, and then use this to find $\rho(u)$ as above.

It was argued [23] that the integrand $\omega\tau/(1+(\omega\tau)^2)$ in (4) is sharply peaked around $\tau = 1/\omega$ and, at least for rather broad spectra, the factor $g(\tau)$ then can be extracted outside the integral which gives

$$g(\tau) = \frac{2}{\pi}\chi''(1/\tau). \tag{8}$$

This would then be a useful first approximation for $g(\tau)$ which is given directly by the loss at the real value $1/\tau$. The relation in (8) is actually an exact asymptotic expression when the relaxation function $\phi(t)$ is a slowly varying function as will be discussed below. For this case also χ' and χ'' as well as $g(\tau)$ are slowly varying. A plausible extension of the simple result above would be a weighted average of χ'' at a few points close to $1/\omega$, i.e.

$$g(\tau) = \sum_{n=0}^{M} h_n\chi''(\xi_n/\tau) \tag{9}$$

with some parameters h_n and ξ_n which have to be determined. In this paper we will show how this expression for $g(\tau)$ can be obtained from the Boas–Widder relation for the inverse Laplace-transform. This gives in general an integral expression for $g(\tau)$, but a straightforward approximation reduces this integral to a sum of χ' or χ'' at a few points. The merit of expressing $g(\tau)$ in terms of the susceptibility for real frequencies is that one can directly use experimental values for these to obtain the spectrum of relaxation times. In a similar way it is possible to use the relaxation function $\phi(t)$ directly to obtain $g(\tau)$.

The interest in obtaining $g(\tau)$ from $\phi(t)$ or $\chi(z)$ is that the former function may contain additional and complementary information about the relaxation processes. The relaxation spectrum $g(\tau)$ can have a sharp cutoff or isolated sharp peaks, even if $\chi''(\omega)$ is rather structureless with a single peak. For very broad spectra where (8) is valid it is clear that $g(\tau)$ contain the same information as the loss spectrum. However when (8) is valid it indicates that $\phi(t)$ is a slowly varying function, and this implies the additional relations

$$\chi'(\omega) = 1 - \phi(1/\omega), \quad \omega \to 0,$$
$$\chi''(\omega) = \frac{\pi}{2}\frac{\partial\chi'(\omega)}{\partial\ln\omega}, \quad \omega \to 0. \tag{10}$$

Therefore for very broad spectra there is a direct relation between the time and frequency dependent functions. The relaxation function is directly given by the real part of the susceptibility or vice versa.

2. Basic theory

Boas and Widder [10] showed that it is possible to invert (1) to find $\rho(u)$ or $g(\tau)$ from the knowledge of $\phi(t)$, and they obtained the exact inversion formula

$$\rho(u) = \lim_{k\to\infty}\int_0^\infty \mathrm{e}^{-ut}P_{2k-1}(ut)\phi(t)\,\mathrm{d}t \tag{11}$$

under the condition

$$\int_0^\infty \rho(u)\,\mathrm{d}u < \infty$$

or equivalently that $\phi(t=0)$ is finite. In our case $\phi(t)$ will be normalized and $\phi(0) = 1$.

Here P_{2k-1} is the polynomial

$$P_{2k-1}(t) = \frac{1}{B(k+1,k-1)}\sum_{p=0}^{k}\binom{k}{p}\frac{(-1)^{k-p}}{\Gamma(2k-p)}t^{2k-p-1}, \tag{12}$$

where $B(x,y)$ denotes the beta-function and Γ is the gamma-function. This gives

$$\begin{aligned} g(\tau) &= \frac{1}{\tau}\rho\left(\frac{1}{\tau}\right) = \lim_{k\to\infty} g_k(\tau) \\ &= \lim_{k\to\infty}\frac{1}{\tau}\int_0^\infty \mathrm{e}^{-t/\tau}P_{2k-1}(t/\tau)\phi(t)\,\mathrm{d}t \\ &= \lim_{k\to\infty}\int_0^\infty \mathrm{e}^{-u}P_{2k-1}(u)\phi(u\tau)\,\mathrm{d}u, \end{aligned} \tag{13}$$

where we introduced

$$g_k(\tau) = \int_0^\infty \mathrm{e}^{-u}P_{2k-1}(u)\phi(u\tau)\,\mathrm{d}u. \tag{14}$$

The polynomial P_{2k-1} oscillates rapidly with increasing k-values. The direct numerical evaluation of (14) is therefore difficult.

We can evaluate the integral and summation over p in (12) analytically in some special cases and then take the